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**CORRELATION BETWEEN THE XPS  
PEAK SHAPES OF  $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$  AND  
FILM QUALITY**



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# Correlation Between the XPS Peak Shapes of $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ and Film Quality

Paul N. Barnes, Sharmila M. Mukhopadhyay, Timothy J. Haugan, Swaminathan Krishnaswami, Justin C. Tolliver, and Iman Maartense

**Abstract**—X-ray photoelectron spectroscopy (XPS) depth profiling was used to investigate the compositional and chemical profile of a typical YBCO coated conductor architecture. Results of the process revealed that the Y(3d) photoelectronic peak shape in these films is very different from bulk YBCO. To investigate this, several samples of  $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$  thin films were intentionally created of varying quality. The films were deposited on  $\text{LaAlO}_3$  by pulsed laser deposition with  $J_c$  values ranging from poorly conducting up to several MA/cm<sup>2</sup>. Initial results indicated a potential correlation between the Y(3d) XPS peak shape (full-width-half-maximum) of the YBCO and the film quality. A potential correlation may also exist with the Cu(2p)/Ba(3d) ratio indicating an interrelationship to the FWHM of the Y(3d) peak. Film quality was determined by current transport, resistive  $T_c$ , and AC magnetic susceptibility measurements.

**Index Terms**—High-temperature superconductors, x-ray photoelectron spectroscopy, YBCO.

## I. INTRODUCTION

SIGNIFICANT progress has been made in the development of the high temperature superconducting (HTS)  $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$  (YBCO) coated conductors [1], [2]. Successful development of the YBCO coated conductor will result in it being available for use in a variety of commercial applications such as power transmission cables, high field magnets, transformers, high power generators and motors, etc. As the next generation HTS conductor, YBCO opens the possibility of even more HTS applications operating at liquid nitrogen temperatures [3]–[5].

These applications require long lengths and a variety of deposition techniques have been successfully developed that show promise of growing such lengths of YBCO thin films having high  $T_c$  and  $J_c$  values. These techniques include pulsed laser deposition (PLD), metal organic deposition (MOD), metal organic chemical vapor deposition (MOCVD), e-beam evaporation, sol-gel, etc. [6]–[11]. However, many improvements can still be made in the properties of the coated conductor as well

as production of longer lengths [12]. Continuing development of the coated conductor necessitates not only a detailed study of deposition techniques, source materials, deposition conditions, and substrates employed, but also characterization of the final deposited films.

Some of the key technical developments and areas include a fundamental understanding of the microstructure and factors affecting current carrying capacity, such as defect tolerant architecture, current limiting mechanisms, microstructure evolution, and process monitoring and control. This particularly requires an investigation of film formation and microstructure evolution for the various types of processing. Although many diagnostic techniques are employed to understand HTS conductors, implementation of additional methods or procedures can help determine unforeseen issues or provide additional insight.

As such, a unique investigation of the chemical and microstructural profiles of YBCO coated conductor samples was conducted using x-ray photoelectron spectroscopy (XPS) [13]. To examine the composition and chemical bonding in the coated conductor architecture, depth profiling of the film was performed using an Ar ion beam sputtering in conjunction with XPS. XPS study previously performed on the YBCO has generally been confined to overall analysis of the near surface region [14]–[17]. However, composition and chemical bonding changes throughout the coated conductor layers and conductor/buffer interfaces are critical to the current carrying capacity as well as the grain boundaries within the film. Therefore, an investigation of chemical and microstructural profiles throughout the HTS conductor deposited under typical PLD conditions for high quality conductors was initiated.

During the course of this study several significant findings were discovered. One of these findings deals with the presence of zirconium in the YBCO when yttria-stabilized zirconia (YSZ) is applied as an underlying buffer layer; these results are being presented elsewhere [18]. Another is the correlation of XPS peak structure to the quality of the deposited YBCO films. It is the initial results of these potential correlations that are presented here.

The Y(3d) photo-electronic peak shape has previously been shown in thin films to be significantly different from YBCO superconductors made by other techniques such as sintering, melt texturing [13]. This is evident in how well resolved the Y( $3d_{5/2}$ ) and the Y( $3d_{3/2}$ ) peaks are where in some cases the full-width-half-maximum (FWHM) of the peaks are very broad. This difference in XPS peak shape might indicate that there are some differences in the atomic coordination between the better quality laser-ablated films and bulk samples made from melt

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solidification. Based on this work, it may well be possible to link the differences in current carrying capacity of the material.

## II. EXPERIMENTAL CONDITIONS

A variety of superconducting samples have been analyzed. These include samples prepared using PLD and MOCVD on both single crystal substrates and on metallic substrates with buffer layers, although primarily PLD of YBCO on single crystal  $\text{LaAlO}_3$  was used for this work. The composition and chemistry of each sample was measured by x-ray photoelectron spectroscopy (XPS) (Kratos AXIS Ultra). Monochromatic Al  $K_{\alpha}$  x-ray line was used for enhanced spectral resolution. The analysis spot size was approximately 110 micrometers. An electron flood charge neutralizer was used during analysis to avoid charge build-up differences between different surfaces (if any).

Most of the samples made consisted of a thin YBCO layer deposited by PLD on single crystal lanthanum aluminate,  $\text{LaAlO}_3$ . The laser ablation was accomplished using a Lambda Physik LPX 305i excimer laser at the KrF transition,  $\lambda = 248$  nm with a 25 ns pulse width. Mounting in the deposition chamber was done with silver paste. Specific details of the deposition conditions are given elsewhere [19]. Some deposition conditions such as temperature and pressure were later intentionally altered to produce poorer quality samples for comparison. Also included in the analysis were a couple samples consisting of YBCO/ $\text{CeO}_2$ /YSZ-sc as well as a YBCO/ $\text{CeO}_2$ /YSZ/inconel sample. The YBCO/ $\text{CeO}_2$ /YSZ-sc samples were created by PLD of a thin ceria cap layer on single crystal YSZ with a final YBCO layer also deposited by PLD. The YBCO/ $\text{CeO}_2$ /YSZ/inconel sample was supplied by an external source with the YBCO being deposited by MOCVD and the YSZ layer by ion beam assisted deposition (IBAD). The YBCO layers were all between 0.2 to 0.6 micrometers thick. The critical transition temperature ( $T_c$ ) of YBCO was measured by ac magnetic susceptibility and the critical current density ( $J_c$ ) by the four-probe transport current measurement.

Ion Beam Sputtering was performed using a mini-beam ion gun.  $\text{Ar}^+$  ions were used at an energy of 3 keV. In the raster setting used, the sputtered area was approximately a 1 mm  $\times$  0.5 mm elliptical region, several times larger than the spot size analyzed by XPS. Spectroscopic analysis was performed on as received surfaces and after subsequent sputter cleaning. A couple of selected samples were "sputter profiled," i.e., a small area was repeatedly sputtered and the freshly exposed surface analyzed after each sputtering. This cycle was continued until the entire thickness of the YBCO film was analyzed and the sputtered crater had reached the buffer layer underneath. This provided information of how the atomic composition and chemistry changed throughout the thickness of the film. Sputtering rate was standardized using a specimen of known thickness.

The ion bombardment process itself can produce some artifacts on complex oxides, such as differential sputtering of some species and crystallinity changes. The main artifact of the ion-beam sputtering process in YBCO is known to be the narrowing of the  $\text{Cu}(2p)$  peak due to chemical reduction of surface copper ions<sup>(15–16)</sup>. In this study, the focus has been

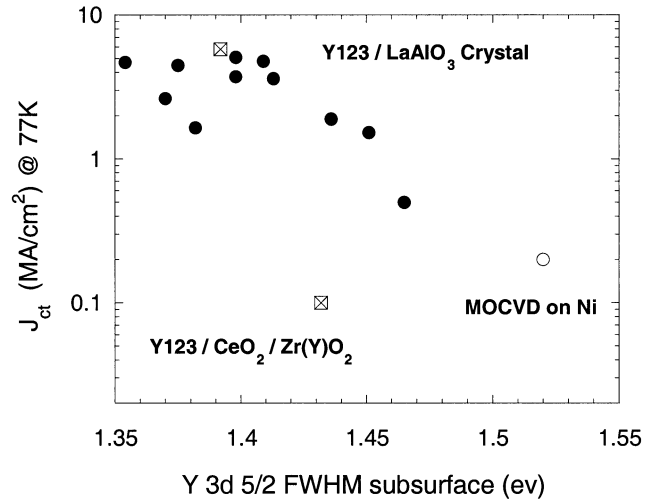


Fig. 1. Correlation of the FWHM for the  $\text{Y}(3d_{5/2})$  peak as determined by XPS and the critical transport current as determined by the four probe resistive technique. The sample preparation methods are labeled in the figure.

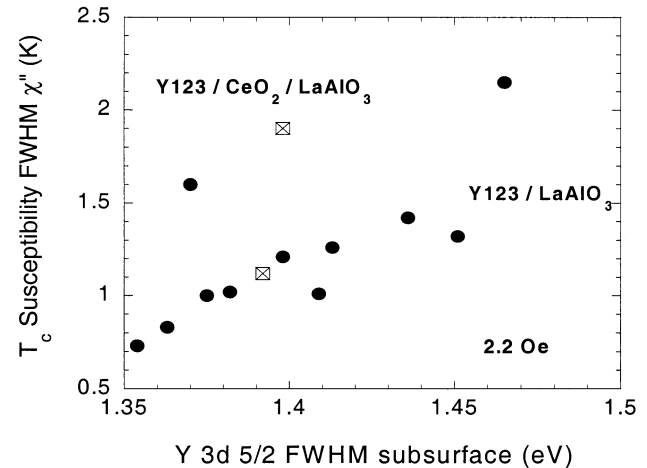


Fig. 2. Correlation of the FWHM for the  $\text{Y}(3d_{5/2})$  peak as determined by XPS and the FWHM of the critical transition temperature as determined by magnetic susceptibility measurements. The sample preparation methods are labeled in the figure.  $T_c$  data determined in 2.2 Oe magnetic field.

on comparing spectra that are all from samples ion bombarded in identical settings. Therefore ion-beam effects such as these should not affect any of the interpreted results.

## III. RESULTS

Photoelectron peaks before and after sputter cleaning indicate that surface composition of as-received samples can be very erratic due to atmospheric degradation. But after 5–15 minutes of ion bombardment (sputter cleaning), the spectra become steady and identical for all samples from the same processing route.

As indicated in Fig. 1, the  $\text{Y}(3d_{5/2})$  photo-electronic peak shape in each of the films varies in FWHM and this variance appears to correlate with the critical transport current of the YBCO films. Although there is some scatter, the general trend is apparent. Even so, this is an initial result and additional data points are required in the  $10^5$  A/cm<sup>2</sup> range and the  $10^4$  A/cm<sup>2</sup> range and below for a stronger verification of this hypothesis.

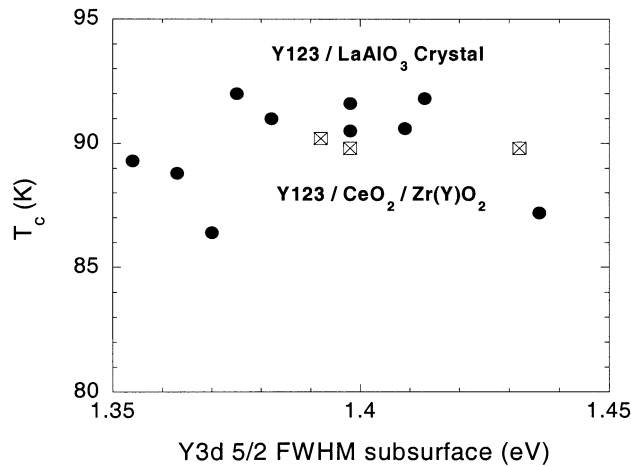


Fig. 3. The critical transition temperature of the samples as determined by magnetic susceptibility measurements are plotted versus the FWHM for the  $Y(3d_{5/2})$  peak as determined by XPS. No clear correlation is evident for the given data.

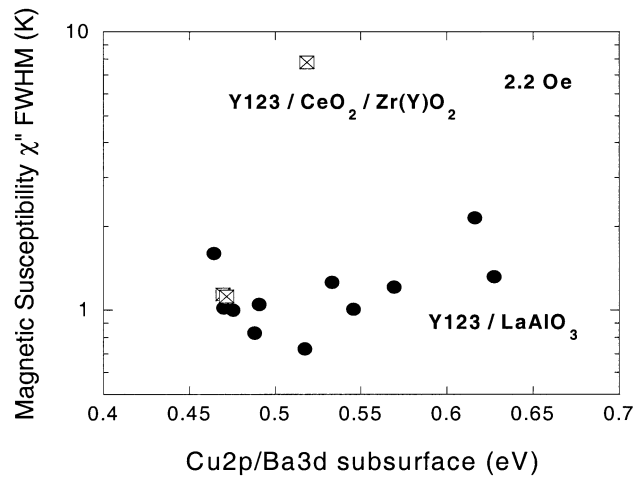


Fig. 5. Correlation of the peak intensity ratios for the  $Cu(2p)/Ba(3d)$  peaks as determined by XPS and the FWHM of the critical transition temperature as determined by magnetic susceptibility measurements.  $T_c$  data determined in 2.2 Oe magnetic field.

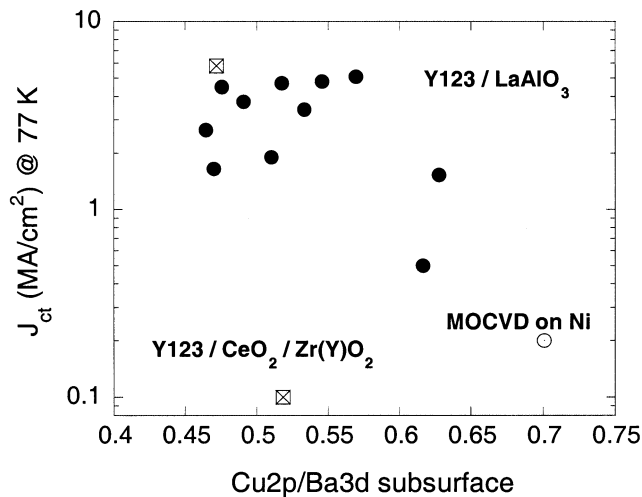


Fig. 4. Correlation of the peak intensity ratios for the  $Cu(2p)/Ba(3d)$  peaks as determined by XPS and the critical transport current as determined by the four probe resistive technique. The sample preparation methods are labeled in the figure.

One notable exception is one of the YBCO/CeO<sub>2</sub>/YSZ-sc samples, being further apart from the others than expected by typical scatter. However, this can be explained in that XPS measurements are not affected by cracks in the YBCO film whereas the critical current transport may well be affected. Currently additional samples are being prepared of lower quality to more fully map out this correlation. If the correlation holds, then the sample can be examined to determine if any cracks are present that have caused a detrimental affect on the current transport measurement.

From Fig. 2, it also seems apparent that in general there is a fairly linear increase of the FWHM of the  $T_c$  curves as determined in AC magnetic susceptibility measurements with an increase in the FWHM of the  $Y(3d_{5/2})$  XPS peak. This is not surprising since a correlation exists between the FWHM of the  $T_c$  ( $\chi''$  of susceptibility measurements) to the critical currents the sample can carry. No real correlation is evident in Fig. 3 between the  $T_c$  of a sample and the FWHM of the  $Y(3d_{5/2})$  peak.

Emphasis must be placed on the fact that these correlations must be further reinforced with additional data and are only preliminary. Even so, sufficient data is present to indicate a strong possibility and are worthy of attention at this point. What may be more surprising, but is less clear, is the potential relationship between the  $J_c$ , as well as the  $\Delta T_c$ , of the deposited YBCO films with the  $Cu(2p)/Ba(3d)$  peak intensity ratios as displayed in Figs. 4 and 5. The scatter displayed in Fig. 4 is significantly greater, but shows a similar relationship with the  $Y(3d)$  peak FWHM. This may indicate a direct correlation between the  $Cu(2p)/Ba(3d)$  peak intensity ratio and the  $Y(3d)$  peak FWHM. The data in Fig. 5 makes this exact relationship unclear though.

#### IV. CONCLUSIONS

A previous observation that the peak shapes of the  $Y(3d)$  photoelectron peak in YBCO thin films are different compared to bulk YBCO specimens has been further investigated in this paper. The XPS photoelectron peaks and cationic concentration profiles of several thin film superconductors have been compared. It is seen that the FWHM of certain peaks as well as cationic peak ratios averaged over the analysis area can vary between differently grown samples. A possible correlation of the FWHM of the  $Y(3d_{5/2})$  XPS peak of YBCO to the thin film quality, specifically the critical transport current  $J_c$ , may exist. A further potential correlation may exist to the  $Cu(2p)/Ba(3d)$  XPS peak intensity ratio. These correlations may well relate to the chemical binding between species. For example, broadening of the FWHM of the  $Y(3d_{5/2})$  XPS peak can indicate alternate undesirable bonding in the YBCO. More data is necessary to fully verify these relationships. If indeed verified, it may offer additional insight into YBCO thin films.

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